Cationic UV Cure Kinetics for Multifunctional Epoxies

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ABSTRACT: Two epoxy monomers with widely different functionalities ($f = 2$ and $f = 8$) were selected for the study and comparison of photocuring kinetics, in the presence of two different photoinitiators. It has been observed that for the same photoinitiator, the optimum concentration is lower for the epoxy monomer with a lower functionality. In terms of photoinitiation efficiency, the photoinitiator based on aromatic sulfonium salts has been determined to be a better candidate. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 518–525, 2002

Key words: monomers; cationic photopolymerization; functionalization; photoinitiator; films

INTRODUCTION

Ultraviolet (UV) and electron beam (e-beam) curing have received considerable industrial and academic attention for rapid, solvent-free curing of polymer films. These solventless polymerizations proceed rapidly at room temperature, with a fraction of the energy requirements of thermally cured systems. To date, most of the work on radiation-initiated polymerizations has focused on free-radical systems based primarily on acrylate and methacrylate monomers. These monomers polymerize rapidly and are easily modified at the ester functionality, allowing materials with a variety of properties to be obtained.[1] However, monomeric acrylates are relatively volatile, have an unpleasant odor, and present potential hazards.[1–4] Oligomeric acrylates are much less volatile but exhibit high viscosities. Finally, free-radical photopolymerizations are inhibited by oxygen and often must be carried out under an inert atmosphere, such as nitrogen.

Radiation-initiated cationic polymerizations exhibit several advantages over free-radical polymerization. Cationic photopolymerization is not inhibited by oxygen and, as such, does not require an expensive setup to blanket the system with nitrogen to obtain sufficiently high cure rates. Also, in contrast to free-radical polymerization, which ceases immediately when the radiation source is removed because of radical–radical termination reactions, cationic reactions proceed spontaneously long after irradiation has ceased and progressively penetrate into recessed areas inaccessible by line of sight to the radiation source. Cationic polymerization has been shown to be applicable to important classes of monomers including epoxies such as the cycloaliphatic epoxies and SU8, a high functionality epoxy-based negative photoresist material that has been extensively used in the photolithographic fabrication of microelectronics machine systems (MEMS).[5–9] These monomers exhibit very low vapor pressures, relatively low viscosities, and negligible toxicity, but polymerize very rapidly to form films that exhibit excellent clarity, adhesion, abrasion resistance, and chemical resistance.

Although the radiation curing of various epoxy systems with differing functionality, including both DEBGA and cycloaliphatic types, have been shown to be efficiently cured using either UV or e-beam, the effect of the functionality on the cure kinetics remains unclear. Little work has been reported relating to fundamental investigations on the curing mechanisms and the kinetics of curing for the UV curing of this epoxy system, although both are prerequisites for the development of process models and for process optimization in the use of the resin.[10–13]

The present study therefore reports on a kinetic study for the UV curing of two epoxy systems with widely differing functionality.

EXPERIMENTAL

The SU8 epoxy resin was obtained from Microchem (Newton, MA). The cycloaliphatic epoxy monomer UVR 6105 was obtained from Union Carbide (Singapore). Two photoinitiators were used. One was composed of a mixture of two sulfonium salts (50 wt % solution in propylene carbonate) purchased from Aldrich Chemical (Milwaukee, WI), the other was a diaryliodonium hexafluoroantimonate salt obtained from Sartomer (Singapore). The solvent used was cyclopentanone from Merck (Darmstadt, Germany). The chemical structures of the materials used in this study are
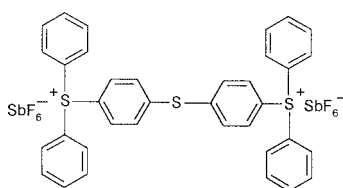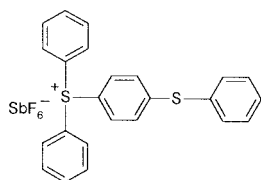

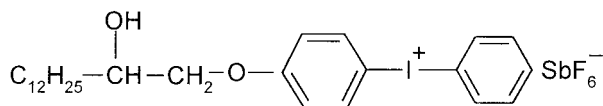*Correspondence to:* F. Boey (mycboey@ntu.edu.sg).
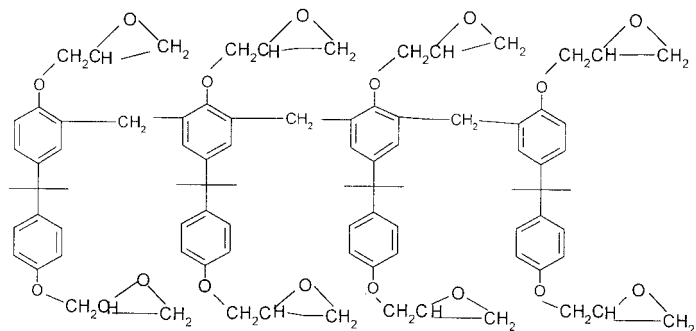
The Chemical Structure of SU8 Epoxy
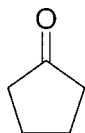Monomer Contains Eight Epoxy Functions
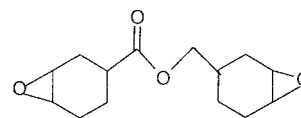
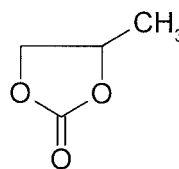A difunctional (f=2)
Cycloaliphatic Epoxy

Components of the Photoinitiator: Mixed Triarylsulfonium/Hexafluoroantimonate

Diaryliodonium Hexafluoroantimonate

Cyclopentanone
(Solvent for SU8)

Propylene Carbonate
(Solvent for Photoinitiator)

Figure 1 Chemical structures of the materials used in this study.

presented in Figure 1. All the chemicals were used as received, without further purification.

The SU8 epoxy was dissolved in cyclopentanone at 70 wt % solids. The photoinitiator(s) added varied from 0.25 to 5.0% of the epoxy solid content. The mixture was stirred with a magnetic stirrer until complete homogeneity was attained and immediately kept in darkness at 0°C before exposure to UV radiation.

The cycloaliphatic epoxy was used in its liquid form with the addition of 0.25 to 5 wt % of the photoinitiators. The mixture was then stirred with a magnetic stirrer until complete homogeneity was attained and immediately kept in darkness at 0°C before exposure to UV radiation.

Characterization of the UV curing was done using a DPC photocalorimeter from TA Instruments (New
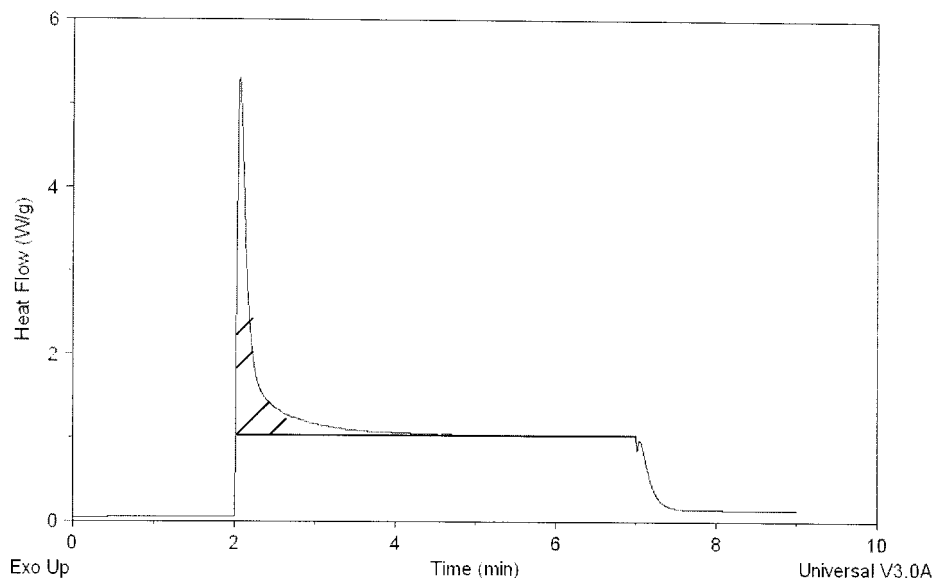
Figure 2 A representative photocuring curve for cycloaliphatic epoxy.

Castle, DE), which was equipped with a 200-W high-pressure mercury lamp, giving an optical range from 285 to 440 nm, with a beam intensity of 5 mW/cm^2. The reference pan used was composed of a fully cured sample of trimethylol propane triacrylate (TMPTA) with a radical photoinitiator, which was exposed under the UV radiation for 20 min. The samples were subjected to 2 min of isothermal conditioning before and after each exposure. The typical exposure time was 5 min. Kinetic modeling of the results was done using the accompanying TA Instruments software.

Both autocatalytic and nth order equations, described as follows, were used to model the reaction exotherms. The autocatalytic model equation has been shown to be described by[10,11]

$$\frac{d\alpha}{dt} = k\alpha^m (1 - \alpha)^n \tag{1}$$

where α is the degree of conversion, k is the rate constant, and m and n are the orders of the various reactions representing the autocatalytic path. The nth order reaction model can be described by[10,11]

$$\frac{d\alpha}{dt} = k\alpha^n \tag{2}$$

Both α and n have the same meaning as in eq. (1), with n representing the order of reaction.
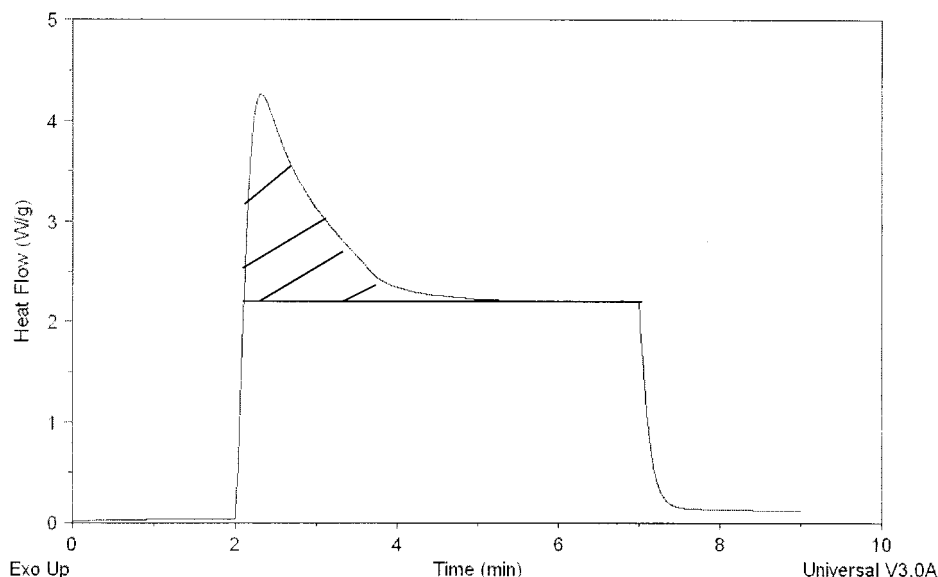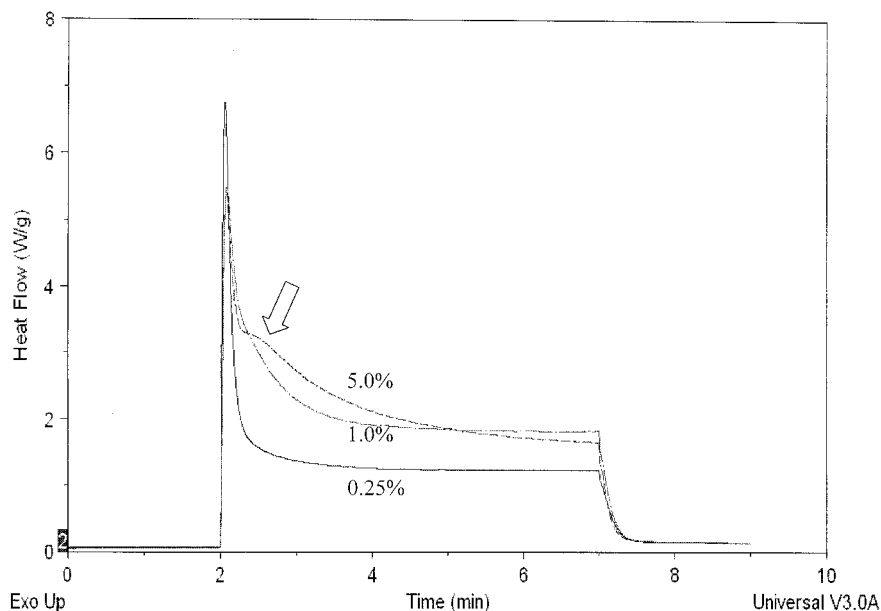

Figure 3 A representative photocuring curve for SU8.

Figure 4 Effect of shape of the exotherm with increasing photoinitiator concentration (cycloaliphatic epoxy with sulfonium salt as photoinitiator).

RESULTS AND DISCUSSION

Figure 2 represents a typical photocalorimetric exotherm obtained for the UV curing of a cycloaliphatic epoxy with 0.25% sulfonium salt. Note that the effective heat of reaction for the UV light is indicated by the shaded area of the exotherm curve above the baseline. Curing is seen to commence immediately upon exposure of the UV, resulting in a very sharp spike followed by an exponential drop. The curing appeared to be completed within 1 min. Figure 3 shows a similar exotherm for SU8 epoxy with 0.25% sulfonium salt. Unlike the cycloaliphatic epoxy monomer, the SU8 epoxy produced a less-pronounced spike followed by a broader exponential drop. Full curing took longer to complete at about 2 min. The difference in the shape and area of the exotherms for the two epoxy monomers may be explained by the difference in functionality between both epoxy systems. The SU8 epoxy moieties are tied up with a relatively rigid aromatic backbone and hence have a different reactivity compared to that of the cycloaliphatic epoxy, where the epoxy groups are attached to cyclohexane rings (which are attached to each with a relatively more flexible grouping: $-COO-CH_2-$). In addition, it is well known that the DGEBA-type epoxies are less reactive than cycloaliphatic epoxies.[7]

Figure 4 presents the exotherms obtained for the cycloaliphatic epoxy with different amounts of sulfonium salt photoinitiator (0.25, 1.0, and 5.0%). All three exotherms showed the expected sharp spike-like peak immediately on exposure, followed again by the exponential drop. It is noted that increasing the amount of photoinitiator in this case resulted in a broadening of the exponential drop after the initial spike. The broadening of the peak indicates that the curing was more spread out and therefore took a longer time for completion. This phenomenon was observed for both photoinitiators used.

A plausible reason for this trend could be attributed to the excess photoinitiator. It is known[3] that cationic polymerizations of the type under discussion are initiated and propagated by the Bronsted acids. The Bronsted acids, in turn, are generated in a series of possible steps involving the excited singlet and triplet states of the photoinitiators. The generalized steps

TABLE I
Results of Exotherms for SU8 and Cycloaliphatic Epoxy

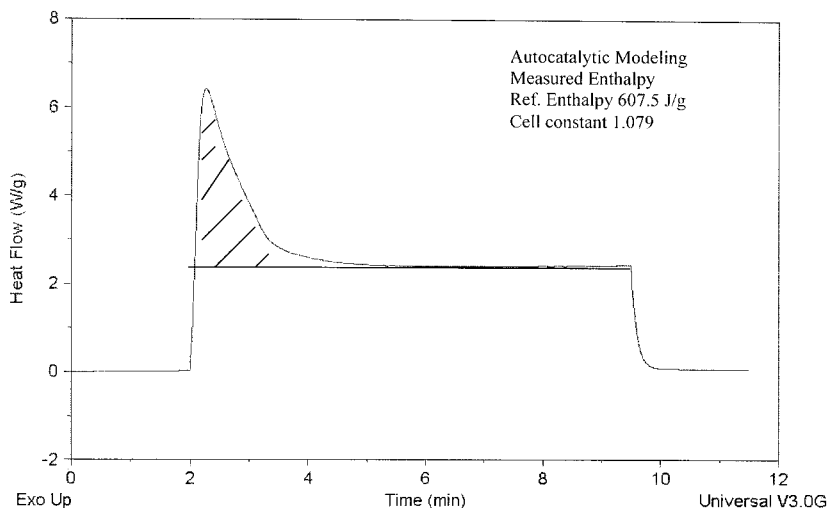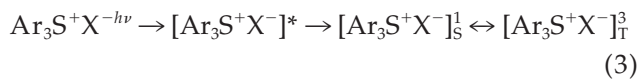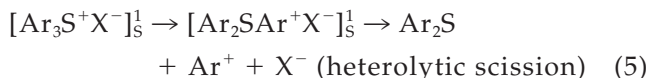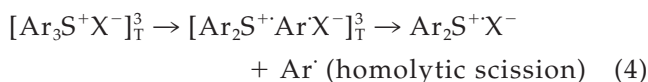| Monomer	Optimum concentration (wt %)	ΔH at optimum concentration	Peak maximum (s)	k (1/min)
SU8				
6974	1.0	303.4	14.4	2.8
1012	3.0	338.1	13.8	3.3
Cycloaliphatic epoxy				
6974	0.5	115.4	4.2	3.57
1012	1.0	235.3	4.2	5.95

Figure 5　A representative plot showing application of autocatalytic modeling.

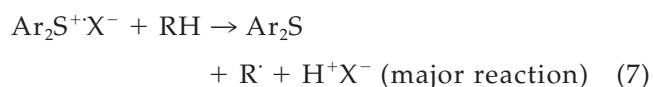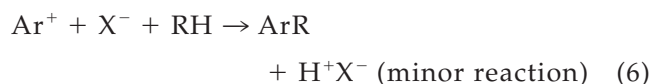(with sulfonium salt as an example) may be visualized as follows.
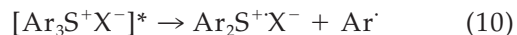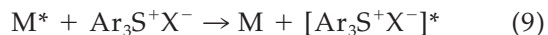
Generation of the excited photoinitiator species

$$Ar_3S^+X^{-hv} \rightarrow [Ar_3S^+X^-]^* \rightarrow [Ar_3S^+X^-]^1_S \leftrightarrow [Ar_3S^+X^-]^3_T \quad (3)$$

Decay of the photoexcited species

$$[Ar_3S^+X^-]^3_T \rightarrow [Ar_2S^{+\cdot}Ar^{\cdot}X^-]^3_T \rightarrow Ar_2S^+X^-$$
$$+ Ar^{\cdot} \text{ (homolytic scission)} \quad (4)$$

$$[Ar_3S^+X^-]^1_S \rightarrow [Ar_2SAr^+X^-]^1_S \rightarrow Ar_2S$$
$$+ Ar^+ + X^- \text{ (heterolytic scission)} \quad (5)$$

The resulting cation-radicals react with small amounts of protogenic and nonprotogenic impurities present in the polymerization media as well as by a variety of chain transfer processes, to give rise to protons in the Bronsted acids, which initiate and propagate the polymerization process[14,15]:

$$Ar^+ + X^- + RH \rightarrow ArR$$
$$+ H^+X^- \text{ (minor reaction)} \quad (6)$$

$$Ar_2S^{+\cdot}X^- + RH \rightarrow Ar_2S$$
$$+ R^{\cdot} + H^+X^- \text{ (major reaction)} \quad (7)$$

In a typical photocurable formulation containing cationic photoinitiator(s) and monomer(s), the bulk of the radiation is absorbed by the monomers, given that the onium salts are present in relatively small concentrations ($\sim$ 1–2%). Upon excitation, the monomers transfer the excess energy to the onium salt. A generalized mechanism under e-beam therefore follows:

$$M \rightarrow M^* \quad (8)$$

$$M^* + Ar_3S^+X^- \rightarrow M + [Ar_3S^+X^-]^* \quad (9)$$

$$[Ar_3S^+X^-]^* \rightarrow Ar_2S^{+\cdot}X^- + Ar^{\cdot} \quad (10)$$

In the present case, the bulk of the radiation is absorbed by the photoinitiator. The broadening effect
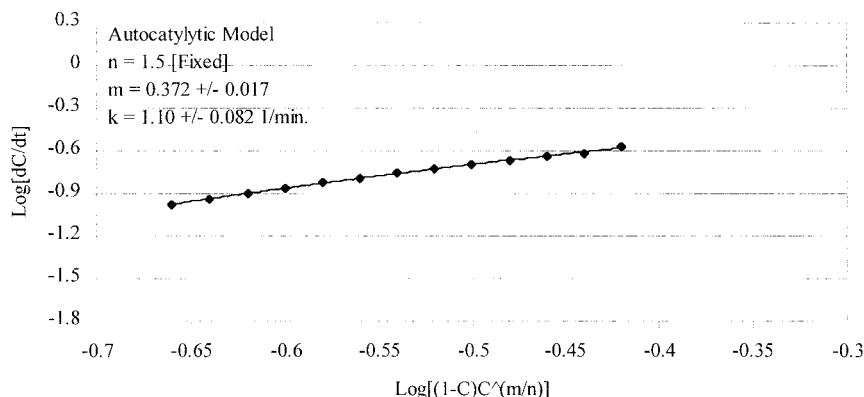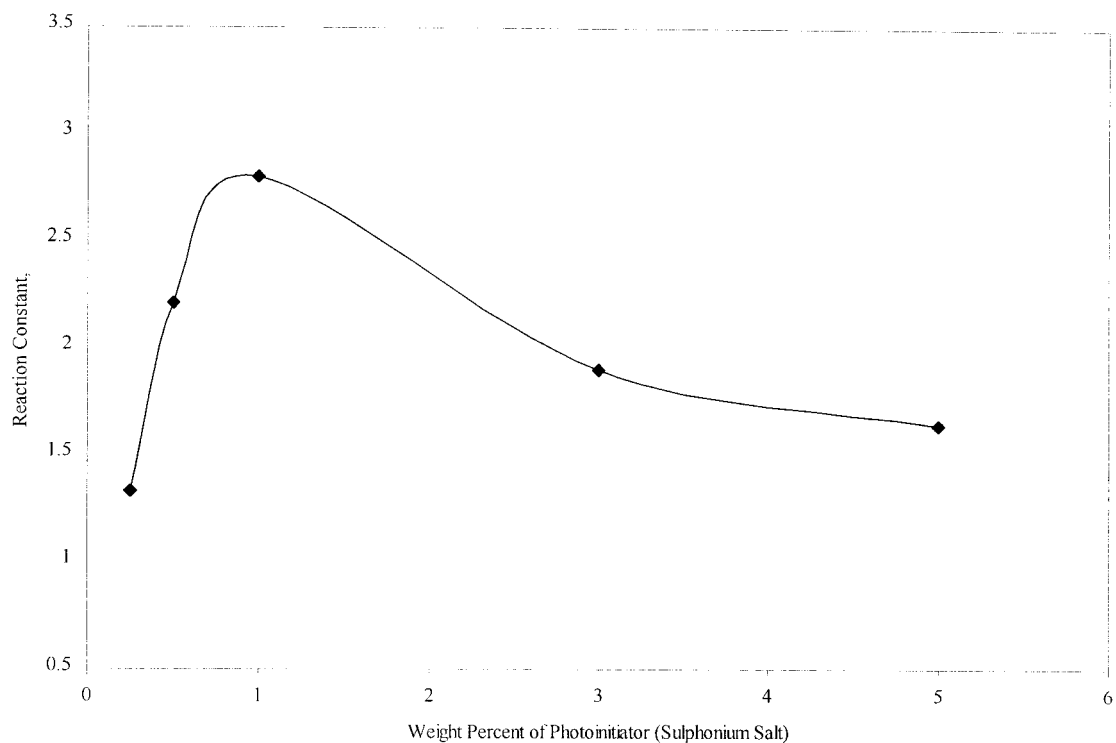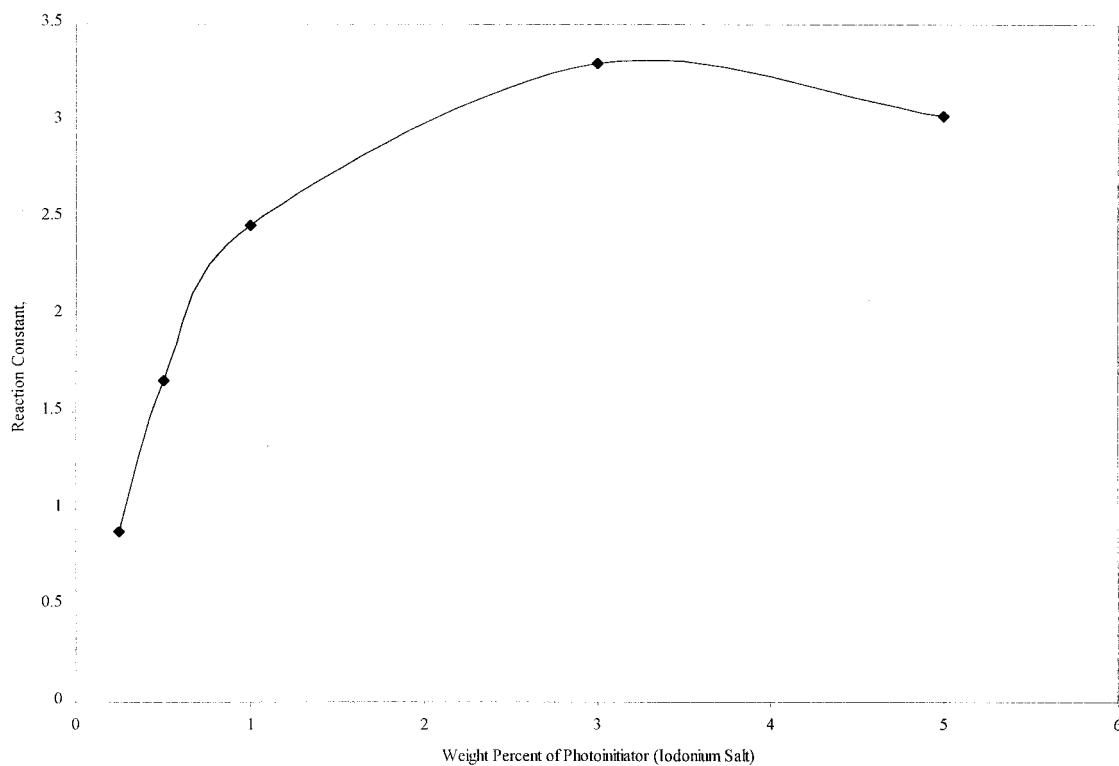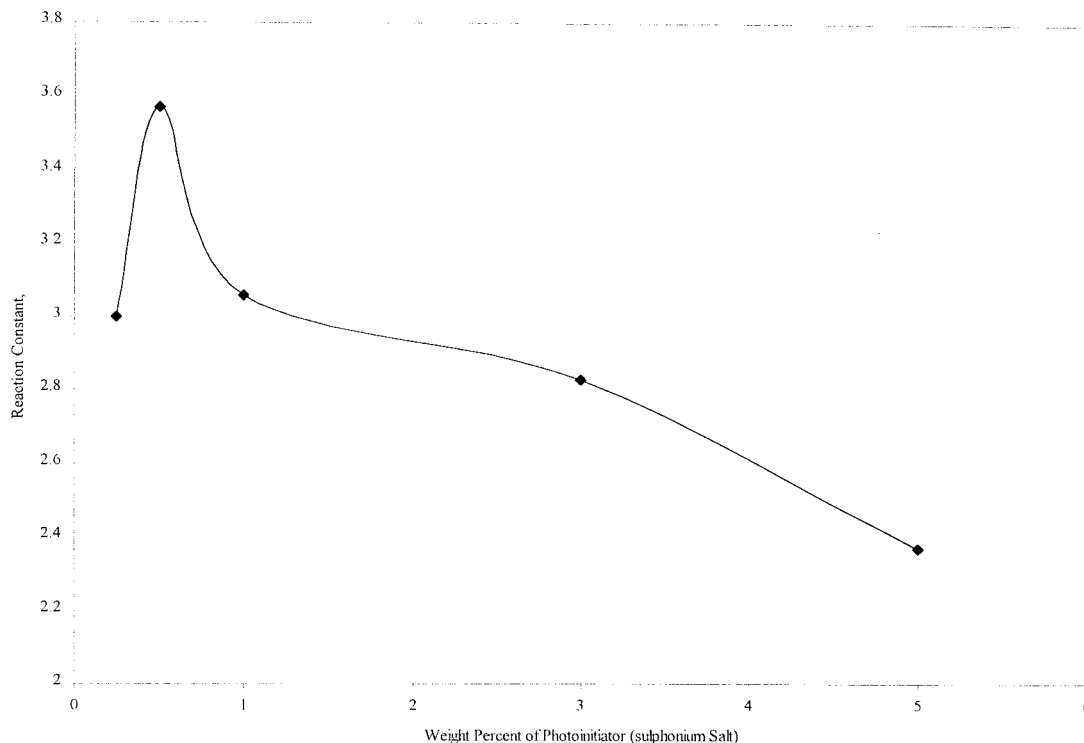

Figure 6　Results of autocatalytic modeling.

Figure 7 Variation of reaction constant k with photoinitiator concentration (sulfonium salt) for the epoxy formulation based on SU8.

with a high percentage of photoinitiator could be the result of decomposition of the photoinitiator, rather than of curing of the resin per se.

Table I tabulates the results of the exotherms obtained for both resins, listing the cure enthalpy under UV exposure, the time at which the peak maximum

Figure 8 Variation of reaction constant k with photoinitiator concentration (iodonium salt) for the epoxy formulation based on SU8.

Figure 9 Variation of reaction constant k with photoinitiator concentration (sulfonium salt) for the formulation based on cycloaliphatic monomer ($f = 2$).

occurs (after exposure starts), and the reaction constant k for the epoxy monomer and photoinitiator combinations, at optimum concentrations. As observed from Table I, the optimum concentration of photoinitiator is always lower for the sulfonium salt than for the iodonium salt, whatever the functionality of the epoxy used. The time at which the peak maximum (the peak maximum corresponds to the maximum rate of cure) occurs differs considerably for SU8 and the cycloaliphatic monomer.

Figures 5 and 6 present the results obtained to model the kinetics of the curing process using the reaction exotherms obtained for curing of SU8 with the sulfonium salt at a concentration of 0.5 wt %. Although both the autocatalytic and nth order models were applied, it was found that the reaction appeared to be better modeled by the autocatalytic path. The reference enthalpy of the epoxy monomers was calculated using the following relationship[16]:

$$\Delta H_{th} = \frac{f \Delta H_{epoxy}}{M} \tag{11}$$

where ΔH_{th} is the theoretical enthalpy of the monomer, ΔH_{epoxy} is the enthalpy of polymerization for the epoxy function (22,600 cal/mol), f is the functionality of the monomer, and M is the molecular weight of the monomer. Thus, a theoretical enthalpy of 607.51 and 749.75 J/g was obtained for the SU8 and cycloaliphatic epoxy monomers, respectively, on the basis of the preceding equation. While applying the autocatalytic

equation, the value of n was kept fixed at 1.5 and the value of $m + n$ at 2. Maintaining fixed values of m and n gave more consistent results.[17]

Figures 7 and 8 present plots of the reaction constant k against the percentage of photoinitiator used, for both sulfonium and iodonium salts in SU8, respectively. It is seen that the optimum photoinitiator concentration for the sulfonium salt was at 1.0%. The addition of iodonium salt, even up to 5.0%, appears to give small increments only to the reaction constant. This clearly establishes that sulfonium salt is a better photoinitiator. A previous report with e-beam curing of the cycloaliphatic epoxy using these two salts as photoinitiators has established the same conclusion.[8]

Figures 9 and 10 present plots of the reaction constant k versus the photoinitiator concentration for the cycloaliphatic epoxy monomer, using both sulfonium and iodonium salts, respectively. In this case, it is seen that both sulfonium and iodonium salts work well to increase the reaction constant, though generally the sulfonium salt appears to be more effective. The optimum photoinitiator concentration for the sulfonium salt is 0.5%, as against 1.0% for the iodonium salt.

CONCLUSIONS

Results show that, of the two photoinitiators with the same counterion, the sulfonium salt acts as a more efficient photoinitiator compared to the iodonium salt. The optimal concentration of the sulfonium salt was found to be 0.5% for the cycloaliphatic epoxy mono-
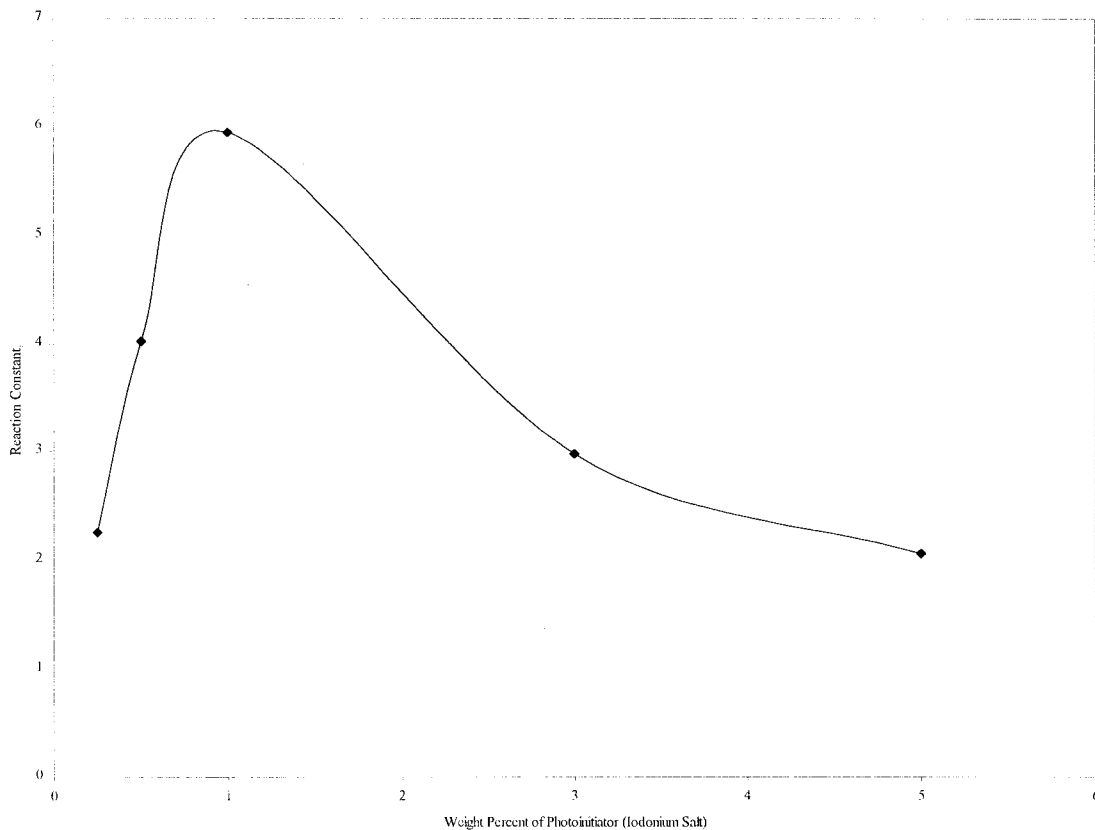
Figure 10 Variation of reaction constant k with photoinitiator concentration (iodonium salt) for the formulation based on cycloaliphatic monomer ($f = 2$).

mer (functionality, $f = 2$) and 1.0% for the high functionality ($f = 8$) epoxy monomer SU8. With the iodonium salt, the optimum concentration was found to be 1.0% for the cycloaliphatic epoxy monomer, whereas it was found to be inefficient for the SU8 monomer.

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